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Dye-Sensitized Solar Cells Using Natural Dyes Extracted From Plumeria and Celosia Cristata Flowers

Siti Noraini Abu Bakar*[1], Huda Abdullah[2], Kamisah Mohamad Mahbor[3]
Shahida Hanum Kamarullah[3]

[1]Faculty of Applied Sciences, Universiti Teknologi MARA, 40450, Shah Alam, Selangor,Malaysia
[2]Department of Electrical, Electronic & System Engineering, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
[3] Faculty of Applied Sciences, Universiti Teknologi MARA Pahang, 26400 Bandar Jengka, Pahang, Malaysia.
**E-mail:noraini.abubakar@gmail.com*

ABSTRACT

In this study, extracted plumeria and celosia cristata flowers have been used as the sensitizer for dye-sensitized solar cells (DSSC). The cells were fabricated using TiO_2 as a semiconductor layer deposited on transparent Indium doped tin oxide (ITO) conductive glass using a spin coating technique. The films with dyes were characterized by UV-VIS absorption spectra. The photovoltaic properties of DSSC were studied under an incident irradiation of 100 mW/cm^2. The I-V characteristic curves of all fabricated cells were measured and analysed. The energy conversion efficiency (η) of the cells consisting of plumeria extract and celosia cristata extract was 3.73×10^{-6} and 1.18×10^{-7}, respectively.

Keywords: *TiO_2 films, natural dyes, spin coating, dye-sensitizer solar cell*

INTRODUCTION

Nowadays, extracting energy from sunlight become one of the most important research areas using photovoltaic. In 1991, O'Regan and Grätzel [1] invented dye-sensitized solar cells (DSSC) that reported as a new type of solar cell. The DSSC is formed of a nanocrystalline metal oxide semiconducting layer deposited on a transparent indium doped tin oxide

(ITO) conductive glass, adsorbed dye on the semiconducting material, counter electrode and an electrolyte containing iodide and triiodide ions.

The working photoelectrode of DSSC is made of transparent conducting oxide substrate and a wide band gap semiconductor film which dye molecules are adsorbed. The sensitizer has an important role in the functioning of DSSC and it mainly defines its performance [2]. The dyes with a broader absorption range and higher molar absorption coefficients are required for efficient light harvesting with TiO_2 film.

The dyes for commercial use are mostly synthetics chemical, such as N719 and N3 dyes, which have satisfactory photoelectric conversion efficiency. These dyes based on ruthenium polypyridyl complexes are used as effective sensitizer, due to their intense charge-transfer absorption in the whole visible range and highly efficient metal-to-ligand charge transfer [3]. However, ruthenium polypyridyl complexes are costly and harmful to the environment [4]. Alternatively, natural dyes can be used for the same purpose with an acceptable efficiency [2-9]. The advantages of natural dyes include their availability and low cost [3].

In this study, organic dyes extracted from two (2) flowers are used to sensitize the TiO_2 film. Red frangipani (Plumeria rubra) and cockscomb flower (celosia cristata) are chosen because of their different content of photoactive. Plumeria rubra contains photoactive anthocyanin while celosia cristata contains photoactive betalain.

Anthocyanins are flavonoids which consist of a benzopyrylium unit linked to a phenyl moiety and one or more sugar. [10]. Anthocyanins are natural compounds responsible for the red-purple colours of various leaves, flowers and fruits. These compounds have also been used as sensitizer for DSSCs [11-13]. Photoactive Betalains, which consist of the yellow betaxanthins and red–violet betacyanins are a group of water-soluble nitrogen-containing alkaloid pigments characteristic of certain members of plant sub-order chenopodineae within caryophyllales and some higher fungi [14]. Like the anthocyanins, the betalains show light absorption in the visible region and are antioxidant compounds [15-17]. The anthocyanins, that present functional groups (–OH), betalains have the requisite functional groups (–COOH) to bind better to the TiO_2 nanoparticles [17-19].

EXPERIMENTAL

Preparation of Natural Dyes Sensitizer

A simple extraction method was employed in order to extract dyes from plumeria and celosia cristata flowers. The fresh flowers was washed using distilled water and dried at 65°C in an oven for about 10 hours to remove the moisture from the flowers. Then the 1 g of the crushed flower was added into 60 mL of 96% ethanol. The mixture was left in a water bath at temperature 40°C for 24 hours to allow the extraction of the dye. The residual of the flower was filtered out. The filtrate was used as the dye solution.

Preparation of the TiO_2 Films

A TiO_2 thin film was prepared based on commercial TiO_2 (Degussa, P25) solution using a spin coating technique. A 0.5 g TiO_2 commercial TiO_2 powder was ground with 1 mL of water and with 1ml of water and 0.1 mL acetylacetone to produce a viscous paste. Then the paste was diluted with slow addition 1.7 ml of water. Finally, 1 drop of Triton X-100 was added to the solution. The resulting solution was spin-coated on pieces of indium-doped tin oxide (InO_2:F, ITO) transparent glass (8 Ω/sq, TEC Glass™) with an area of 10 × 10 mm^2 at a rate of 2000 rpm for 30 seconds. The film is annealed in furnace at 450°C for 60 min.

Assembling of Dye-Sensitized Solar Cells

The conductive glass TiO_2 film was immersed in an alcoholic solution of natural dyes sensitizer and ethanol-based commercial N719 (Sigma-Aldrich) dye solution for 24 h to adsorb the dye on the TiO_2 porous film adequately. The TiO_2 film electrode and a conductive glass sheet plated with platinum (Pt) counter electrode were sandwiched and sealed by using a Surlyn (Dupont) thermoplastic frame (25 μm thick) to assemble the DSSC. The space between the two electrodes was filled with a commercial electrolyte purchased from Solaronix (Iodolyte AN- 50, Switzerland). Then the two electrodes were clipped together to form a solar cell.

Measurements

The film crystallinity was analysed with X-ray diffraction Diffractometer (Siemens D-5000) with CuKα irradiation (λ=1. 5406 Å). The absorption spectra of thin films were obtained using an ultraviolet-visible (UV-Vis) 900 Lambda Spectrometer (Perkin-Elmer, Wellesley MA, USA). Photovoltaic IV curve experiment has been performed using GAMRY INSTRUMENTS G300 using physical electrochemistry software under simulated AM 1.5G solar illumination using a 100 mW/cm^2.

According to the I-V curves, the fill factor (FF) was calculated as:

$$FF = I_m V_m / I_{sc} V_{oc} \quad (1)$$

where I_m and V_m are the photocurrent and photovoltage for maximum power output (P_m), I_{sc} and V_{oc} are the short-circuit photocurrent and open circuit photovoltage, respectively.

The overall energy conversion efficiency (η) is defined as:

$$\eta = FF I_{sc} V_{oc} / P_{in} \quad (2)$$

where P_{in} is the power of incident light.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) analysis by X-ray Diffractometer (Siemens D-5000) with CuKα irradiation (λ=1. 5406 Å) was used to analyze the orientations of TiO_2 thin film crystalline. Figure 1 shows the XRD spectrum of TiO_2 film after annealed at 450°C for 60 minutes. The XRD analysis shows that the crystal structures for all thin films are composed of anatase and rutile phases. This result was obtained after comparing the thin film XRD pattern with the standard spectrum of JCPDS file No: 01-078-2486 (TiO_2-anatase) and No: 01-086-0147 (TiO_2-rutile). The peaks appeared at 2θ values of 25.319°, 37.840°, 48.040° corresponds to the crystal planes of (101), (004) and (202) for TiO_2 anatase. On the other hands the values of 27.440° and 1.667° correspond to the crystal planes of (110) and (211) for TiO_2 rutile.

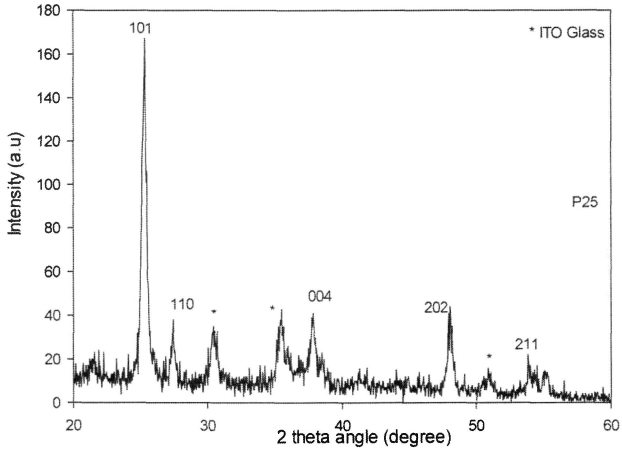

Figure 1: XRD spectrum of TiO_2 film after annealing at 450°C for 60 minutes

Figure 2 shows the UV-VIS absorption spectra of plumeria (A) and celosia cristata (B) using ethanol as solvent. It was found that the absorption peaks of plumeria (A) are about at 390 nm and 550nm. For celosia cristata (B) the peak of absorption is at 320nm. An absorption peak at high wavelength of plumeria (A) is responsible for its red colour [20].

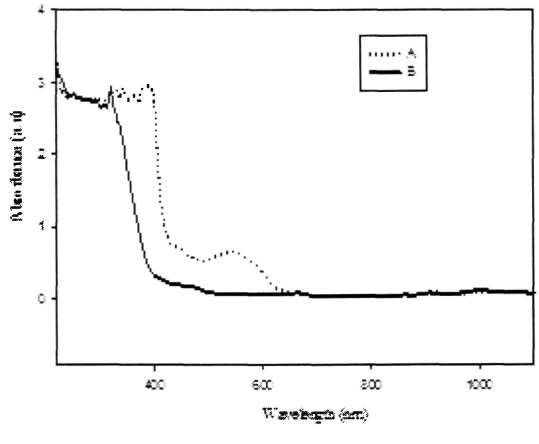

Figure 2: Absorption spectra of the extracts of plumeria (A) and celosia cristata (B) using ethanol as solvent

The absorption spectra of photoanode after immersion are shown in Figure 3. The absorption peaks of photoanode are broader than the dye solution. The difference in absorption peak is due to the binding of anthocyanins and betalains in the extract to the oxide surface [21]. For plumeria (A), the peak is shifted to a higher wavelength from 390 nm to 480nm and 550 nm to 570 nm. Also for celosia cristata (B) the peak is shifted from 320nm to 480nm. The commercial dyes N719 showed an absorption peak at 490 nm and 560 nm. From the results, comparing the natural dyes, plumeria (A) is more adsorbed onto TiO_2 film than celosia cristata (B) based on the absorption peak. Plumeria (A) and commercial dyes N719 the absorption peaks almost at the same wavelength.

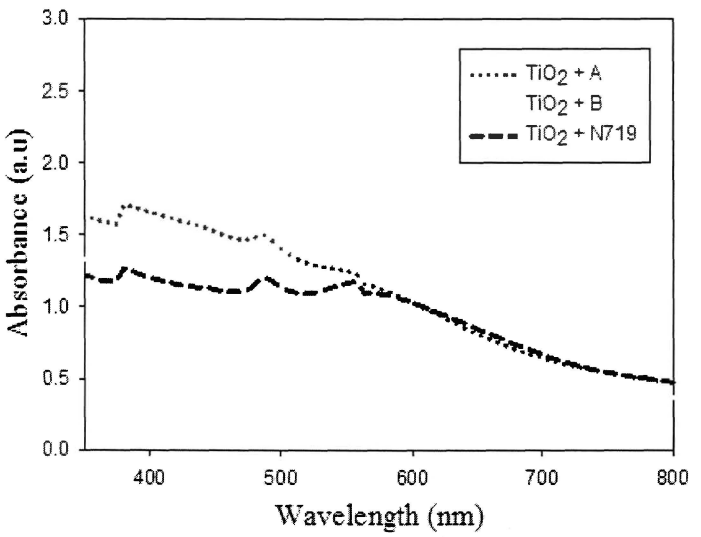

Figure 3: Absorption spectra of TiO_2 film after immersion with the dyes for 24 hours

Figure 4 shows the I-V (current-voltage) curve for DSSC sensitized by plumeria (A), celosia cristata (B) and commercial N719 at light intensity 100 mW/cm^2. Table 1 presents the parameters of DSSCs sensitized by different dyes. The DSSCs output power has been calculated as $P = I V$ using the I-V data corresponding to each cell. The photocurrent (I_m) and photovoltage (V_m) corresponding to the maximum power point (P_m) were obtained for each cell. The values of the fill factor (FF) and the cell conversion efficiency (η) were then calculated using equation (1) and (2).

The values of the fill factor the cell conversion efficiency were calculated. Results were summarized in Table 1. As seen from the Table 1, the short circuit density is 3.91 $\times 10^{-3}$ mA/cm^2, 2.53 $\times$ 10^{-4} mA/cm^2 and 1.48 $\times$ 10^{-1} mA/cm^2 for plumeria (A), celosia cristata (B) and commercial dyes respectively. The J_{sc} for plumeria (A) is higher when compared to celosia cristata (B). This indicates the better charge transfer to TiO_2 nanoparticles. The open circuit voltage for plumeria is 0.29 V, celosia cristata is 0.1 V and commercial dyes N719 is 0.67 V. While the fill factor is 0.329 %, 0.467 % and 0.579 % for plumeria, celosia cristata and commercial dyes N719, respectively. For the cell conversion efficiency, plumeria have slightly higher efficiency value than celosia cristata, 3.73 $\times$ 10^{-6} and 1.18 $\times$ 10^{-7} respectively. The value of cell conversion efficiency for commercial dyes N719 is 4.80 $\times$ 10^{-4}. The plumeria (A), which the photoactive anthocyanins has shown a better efficiency compare to Betalain the photoactive in celosia cristata.

It is noted that efficiency of the DSSC sensitized by N719, under the same condition with natural dyes is 4.80 $\times$ 10^{-4}. When compared the natural dyes to the commercial dye, the efficiency of natural dyes still lower than that of the commercial dye.

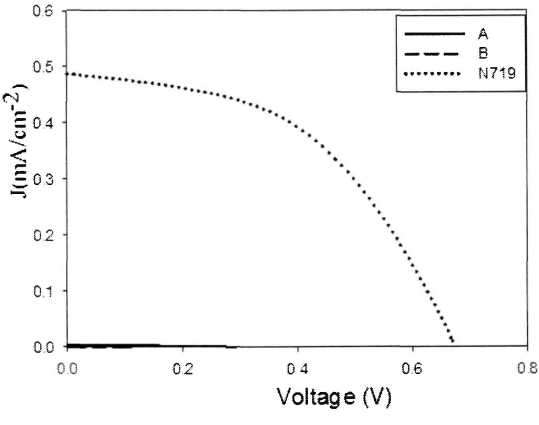

Figure 4(a)

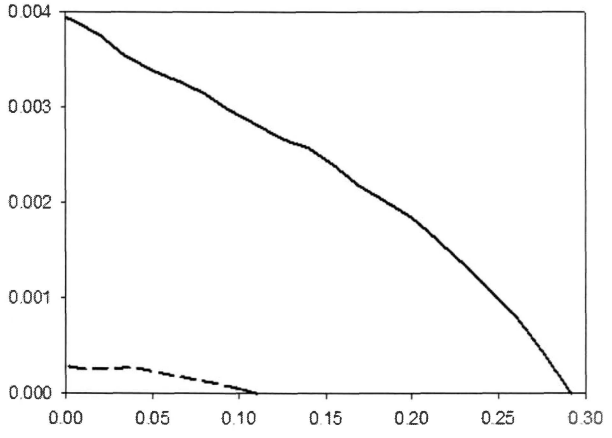

Figure 4(b)

Figure 4(a) & (b): I-V curves for DSSC sensitized by plumeria (A), celosia cristata (B) and commercial N719 at light intensity 100 mW/cm²

Table 1: Parameter of DSSC from different dyes

Dye	J_{sc} (mA/cm²)	V_{oc} (V)	P_{max} (mW/cm²)	FF %	η %
Anthocyanins (A)	3.91×10^{-3}	0.29	3.72×10^{-7}	0.329	3.73×10^{-6}
Betalains (B)	2.53×10^{-4}	0.10	1.18×10^{-5}	0.467	1.18×10^{-7}
Commercial N719	1.48×10^{-1}	0.67	4.80×10^{-2}	0.579	4.80×10^{-4}

Figure 5 shows the electrochemical impedance spectra of different dyes using plumeria, cristata and commercial N719. The analysed data are summarized in Table 2. In general, Electrochemical Impedance Spectra (EIS) of DSSC exhibits three (3) semicircles. The semicircle developed at high frequency region is due to the charge transfer at the counter electrode. The semicircle developed at intermediate frequency region due to the TiO_2/ dye/electrolyte interface and the semicircle developed at low frequency region is attributed to the diffusion in redox electrolyte.

The charge transfer resistance (R_{pt}) are 741.7 Ω, 3.36 Ω, and 1188.0 Ω and the charge transfer in the TiO_2/dye/electrolyte interface resistance

(R_{ct}) is 212.6 Ω, 37.15 Ω, and 97.82 Ω corresponding the DSSC based on plumeria, celosia cristata and N719 respectively, as shown in Table 2. The different of results for R_{pt} and R_{ct}, is caused by the binding between the dye molecules and the TiO_2 film. R_s is denoted as sheet resistance of the conducting glass. The value of R_s is 544.4Ω, 95.44 Ω and 140.10 Ω for plumeria (A), celosia cristata (B) and commercial dyes N719, respectively. For the R_t is the electron transport resistance from the TiO_2 photoanode. R_t for plumeria (A) is 281.10 Ω, for celosia cristata (B) is 55.97 Ω and for commercial dyes N719 is 1101 Ω.

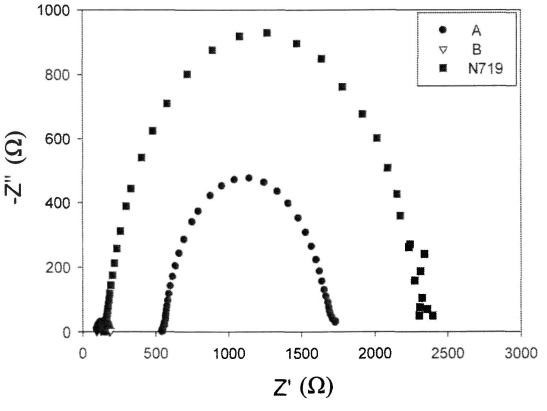

Figure 5(a)

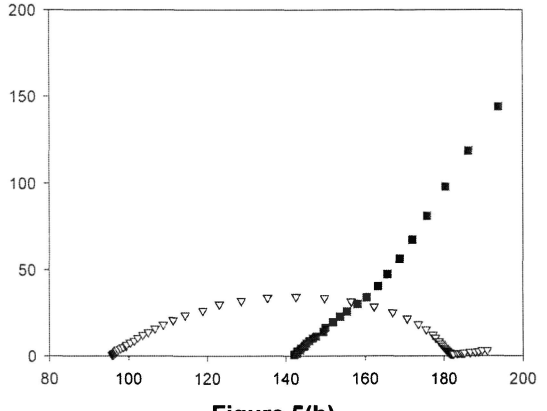

Figure 5(b)

Figure 5(a) & (b): Electrochemical impedance spectra of plumeria (A), celosia cristata (B) and commercial N719

Table 2: Results of the impedance analysis for DSSC using different dyes as sensitizer

Dye	R_s (Ω)	R_{ct} (Ω)	R_t (Ω)	R_{pt} (Ω)
Plumeria (A)	544.40	212.60	281.10	741.70
Celosia Cristata (B)	95.44	37.15	55.97	3.36
Commercial N719	140.10	97.82	1101	1188

CONCLUSION

In this study, anthocyanins and betalains were successfully extracted and used as the sensitizer for DSSCs application. In conclusion, the plumeria (A) extract has higher photosensitized performance when compared to celosia cristata (B) extract. This is due to a better charge transfer between plumeria (A) dye molecule and the TiO_2 surface.

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